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Micro-Tribological Performance of MoS_2 Lubricants with Varying Au Content

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Micro-tribological performance of MoS_2 lubricants with varying Au content

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ABSTRACT

Microtribological testing with a spherical diamond tip (radius = 100 µm) was conducted on two Au–MoS_2 coatings with 32 at.% and 84 at.% Au. For lower loads (0.2 to 2.0 mN), the performance of both coatings was similar, with minimal wear (<50 nm depth) and relatively stable friction coefficients. At higher loads (3.0–5.0 mN), similar trends were found for the 84 at.% Au specimen, but the 32 at.% Au sample wore severely and the friction became unstable. Non-linear curve fitting of friction coefficient versus normal load was conducted using a model containing an elastic (Hertzian) term and a plastic (plowing) term. Changes in the two contributions to the friction with time were used to explain the differences in performance observed between the two coatings.

1. Introduction

Solid lubricant coatings typically have a specific range of environmental and engineering conditions over which they are most effective. Many of these variables are well known (humidity, temperature, roughness, counterface material, etc.) and tribological performance has been characterized with them in mind for many years. More recently, with the advent of micro-electromechanical systems (MEMS) and a desire to use solid lubricants for these applications [1], the variables of contact size and stress have become more important. More specifically, it remains unclear how a reduction in contact size will affect the viability of these materials, including their ability to self lubricate by the formation of transfer films [2].

Experimental efforts in this area may be sub-divided into two regimes: testing conducted on real MEMS devices that are constructed as miniature tribometers [3,4], and those that simulate the conditions for a real device through micro- and nanotribological testing [5–8]. Both paths have pros and cons. The first, while able to provide conditions virtually identical to a real device, requires extensive investment in making the devices, which always have some finite yield from their microfabrication. Furthermore, any desired changes in contact size or material require additional devices to be made. For the second path, there are always questions on how accurately the experimental technique, such as atomic force microscopy (AFM), nanoindentation or microtribometry, simulates the contact conditions in MEMS. However, because tribology and lubrication are not well understood at these length scales, the ability of these techniques to more easily change contact conditions (size, chemistry, etc.) makes them a useful alternative that provides insight on the metrics that control friction at the reduced length scales of MEMS.

The microtribology of two Au–MoS_2 coatings with 32 and 84 at.% Au was studied with a nanoindentation instrument equipped with scratch capability. These coatings, depending on the Au content, were recently found to have good performance in macrotribology testing across a wide range of contact stresses [9]. In this study, the contact size is reduced while maintaining a similar contact stress, allowing an exploration of the potential of these coatings for MEMS and other microtribological systems (e.g. electrical microswitches). Sliding wear experiments were conducted in a dry environment, and the contact size and stress were varied by changing the normal load. The friction results were analyzed using a combination of Hertzian elastic model and an additional plowing term. This analysis combined with wear measurements provided insight on the necessary contact conditions and preferred coating composition to provide lubrication for micro-scale sliding contacts.

2. Experimental procedure

Nanocomposite coatings of Au and MoS_2 were co-deposited in a high vacuum chamber onto polished Si wafers. Separate Au and MoS_2 rf-magnetron sputtering sources were used, with Ar as the sputtering gas. More details for the specimen preparation are found in the literature [9]. The composition of the coatings was measured by Auger spectroscopy (PHI 680 Auger Nanoprobe). Atomic force microscopy (Nanoman or Dimension 3100, Veeco) was used to determine the coating thickness from step-height measurements and the roughness from 20×20 µm^2 scans of the unworn coating.

Nanoindentation and sliding wear tests were performed using an instrumented indenter with a lateral force option (Hysitron TriboIndenter). A sphero-conical tip with a radius of 100 µm was used for the

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sliding tests and a Berkovich tip was used for the nanoindentation tests. Prior to the experiments, the area functions for both tips were determined from indentation on fused quartz. The hardness and elastic modulus of the coatings were determined from nanoindentation tests using a standard Oliver and Pharr analysis [10]. Between ten and twenty indentation tests were conducted for each coating that resulted in contact depths between 10 and 50 nm (between 3 and 16% of the total coating thickness). The results from these tests were used to determine the average mechanical properties.

Sliding tests were performed under controlled temperature of 22 °C and a relative humidity of 4.0±0.2%. The relative humidity was controlled by flowing nitrogen gas, which passed through a desiccant (anhydrous $CaSO_4$) and into the instrument enclosure at a high flow rate for 10 min and then a constant low flow rate throughout the sliding experiments. The friction results from the sliding experiments were analyzed using a custom-built analysis code with Matlab, Version 7.5.0. Wear depth measurements were determined from line profile measurements across wear track images acquired by AFM.

The sliding experiments were conducted with 8 μm track lengths at a constant velocity of 4 μm/s. The normal load used for the experiments was 0.2, 0.5, 0.7, 1.0, 2.0, 3.0, and 5.0 mN. The total number of sliding cycles was 800, but due to limitation on the instrument software, the experiment consisted of “test cycles” of 40 sliding cycles each that were repeated twenty times consecutively at the same position. Each test cycle consisted of three phases, 1) a pre-scan, to image the topography at a 20 μN load, 2) an oscillating scratch, where the sample is worn under a high constant load for 40 sliding cycles, and 3) a post-scan with 20 μN load to image the topography of the resulting wear trace [6,8]. A plot of the normal force and lateral position versus time is presented in Fig. 1 for a test cycle with a normal load of 0.5 mN. In between test cycles, the tip briefly leaves the surface of the specimen and then re-engages with the surface at a small force (~2 μN). The tip then remains stationary at the center of the wear track for approximately 90 s while the next test cycle is loaded in the software. Based on the specifications of the instrument and images of wear tracks, any misalignment upon re-engaging the test is on the order of a few nanometers.

The coefficient of friction was calculated from the lateral force divided by the normal force. The average friction coefficient for each cycle was calculated from 39 data points corresponding to the central 5 μm of the track. Custom-built analysis code was used to conduct non-linear curve fitting of friction data versus normal load. This fitting was conducted for data near the end of each test cycle to investigate the evolution of both the Hertzian (elastic) and plowing (plastic)

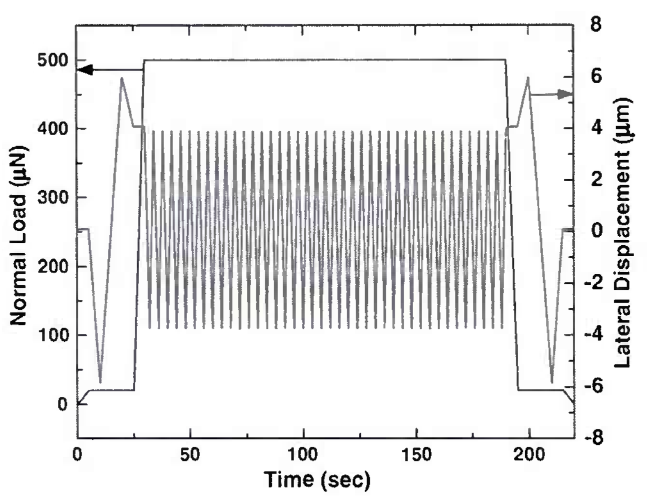

Fig. 1. Normal load (black) and lateral displacement (gray) versus time for a test cycle with a normal load of 0.5 mN.

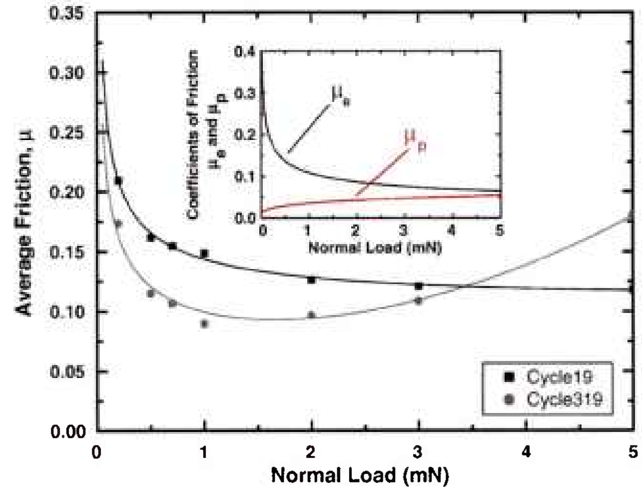

Fig. 2. Average coefficient of friction versus normal load, fitted using a combination of Hertzian elastic model and an additional plowing term (see Eq. (1)) for the 19th cycle on the MoS_2/84% Au and 319th cycle on the MoS_2/32% Au sample. The inset shows the typical shape of the elastic (μ_e) and plastic (μ_p) components.

contributions to the total friction as a function of time. The equation used to model the two contributions was:

$$\mu = \mu_e + \mu_p = c_1 L^{(-1/3)} + c_2 L^m \quad (1)$$

where the first term is the Herztian contribution and the second term is the plowing component. This equation has been used by Schiffman and Hieke for similar sliding wear experiments on diamond-like carbon materials [8]. The fitting constant c_1 in Eq. (1) may be written as

$$c_1 = S\pi(3R/4E)^{(2/3)} \quad (2)$$

where R is the radius of the spherical counterface, S is the shear stress and E is the reduced modulus of the contact [11]. The plowing portion of Eq. (1) is largely empirical, but can be considered to have c_2 inversely proportional to yield strength and the exponent, m, related to both yield strength and a strain hardening index [8].

Fig. 2 is an example of data for friction coefficient versus normal load where either the elastic or the plastic part of Eq. (1) is dominating. When the elastic part dominates, the curve has a smooth drop in friction with normal load, which matches closely to an $L^{-1/3}$ dependence (see inset in Fig. 2 as well). When the plastic part of the sliding process has a significant effect, the data at higher loads typically have higher friction coefficients. In both cases, and for those in between, Eq. (1) was found to confidently fit the friction measurements versus load as shown in Fig. 2.

3. Results

3.1. Coating properties

The two coatings studied here had compositions of 32 and 84 at.% Au. The thickness and RMS roughness of the coatings were found to be nearly identical (see Table 1). The mechanical properties of the

Table 1
Properties of MoS_2/Au coatings

Sample	Thickness (nm)	RMS roughness (nm)	Modulus, E (GPa)	Hardness, H (GPa)	H/E
MoS_2/32 at.% Au	310	6.3	43±11	1.1±0.3	0.025
MoS_2/84 at.% Au	320	4.7	88±18	2.0±0.4	0.022

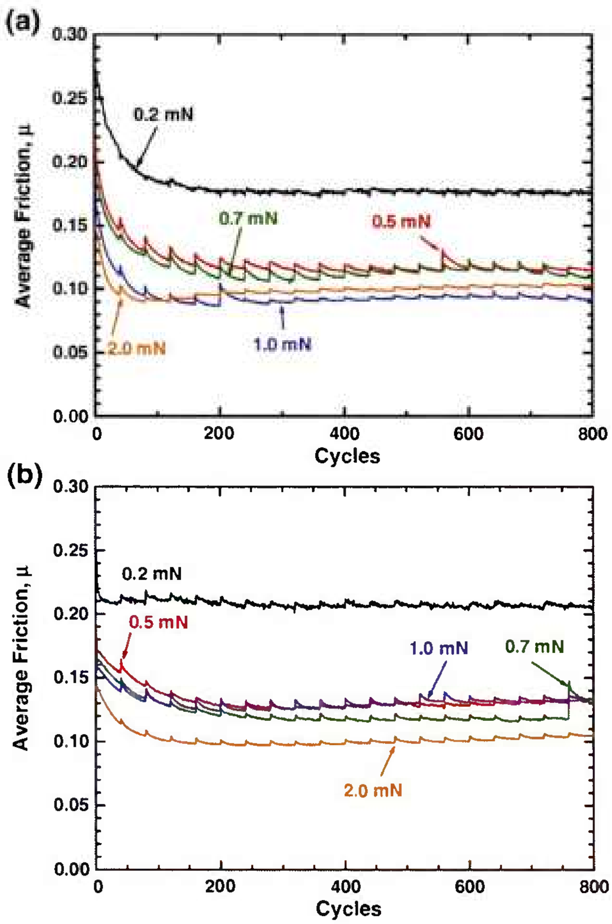

Fig. 3. Average friction versus cycles for the MoS_2 coating with 32 at.% Au (a) and 84% Au (b) for normal loads from 0.2 mN to 2.0 mN.

coatings as determined by nanoindentation are contained in Table 1. The 32% Au coating was found to be softer and less stiff than the 84% Au coating. However, the *H*/*E* ratios for the two coatings were nearly identical.

3.2. Friction performance

For normal loads between 0.2 and 2.0 mN, both the 32% Au coating (Fig. 3(a)) and 84% Au coating (Fig. 3(b)) exhibited a rather smooth run-in to friction coefficients between 0.1 and 0.18. In general, larger loads resulted in a smaller friction coefficient. Also, for most tests, there was a rise in the friction coefficient every 40th cycle, which coincided with the re-initiation of a subsequent test cycle. The friction rise could be due to numerous effects that might occur during a halt to sliding, such as: 1) adsorption of water vapor and mild oxidation of the wear track, 2) de-bonding of the transfer film or 3) a small misalignment of the tip upon re-initiation of the test cycle. To examine possible oxidation, experiments were conducted with increased time between test cycles. It was observed that the friction rises did not increase in magnitude with longer wait times. Based on this result and the observed low error in tip misalignment, our current understanding is that disturbance of the transfer film, probably during pre- and post-scanning (see Fig. 1), is the mechanism having the greatest effect on the friction rises. While the friction rises are unavoidable due to instrument limitations, their ultimate effect was found negligible on the eventual steady state friction behavior. This was confirmed by recent tests with an upgraded instrument allowing an increased number of sliding cycles. Similar run-in and steady state behavior without friction rises was observed for tests without pauses every 40 cycles.

For higher normal loads of 3.0 and 5.0 mN, the friction behavior of the 84% Au coating (Fig. 4(b)) was similar to the behavior at smaller loads. However, higher load experiments on the 32% Au specimen resulted in markedly different behavior (Fig. 4(a)). For a load of 3.0 mN, a steady state friction of 0.1 is obtained after roughly 50 sliding cycles, but by cycle 300, the friction started to rise and was 0.17 by the end of the test. For a load of 5.0 mN, the friction coefficient started at approximately 0.14, rose steadily and then varied between 0.16 and 0.24 for the remainder of the test.

3.3. Wear

Wear depth measurements were obtained from AFM images of the wear tracks after 800 sliding cycles. Two line profiles were drawn across each wear track and an average was taken. Fig. 5 is a plot of the wear depth versus the normal load for both coatings. For smaller normal loads between 0.2 and 1.0 mN, the wear depths for the two coatings are nearly identical. At higher normal loads between 2.0 and 5.0 mN, the wear for the 32% Au coating was greater than the 84% Au coatings. The difference in wear between the two coatings becomes greater with increasing normal load. All wear depths were less than the measured coating thickness except the 5.0 mN load test on the 32% Au coating, which has a wear depth of 350 nm, compared to the

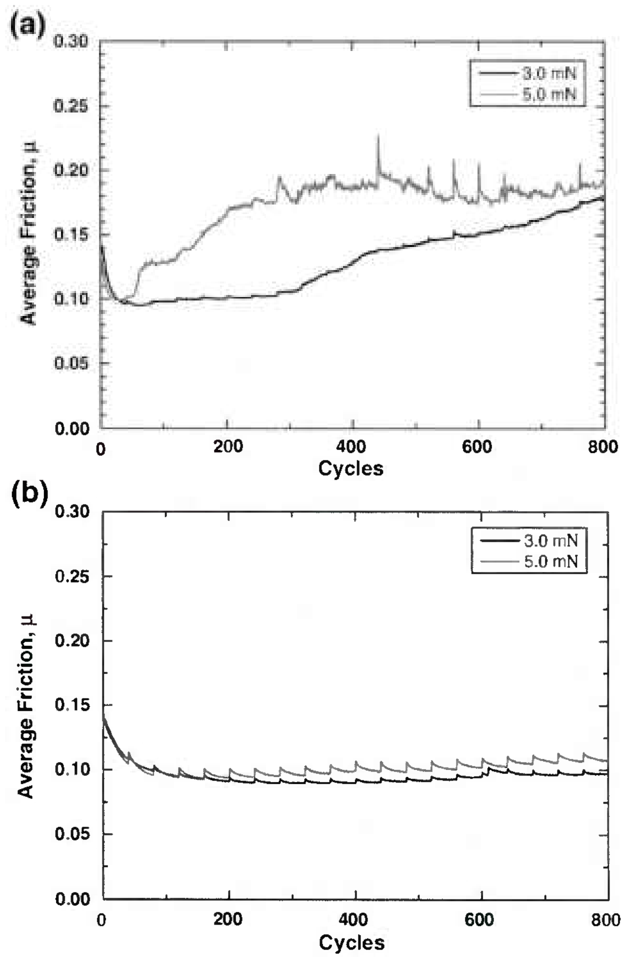

Fig. 4. Average friction versus cycles for the MoS_2 coating with 32 at.% Au (a) and 84 at.% Au (b) for normal loads of 3.0 and 5.0 mN.

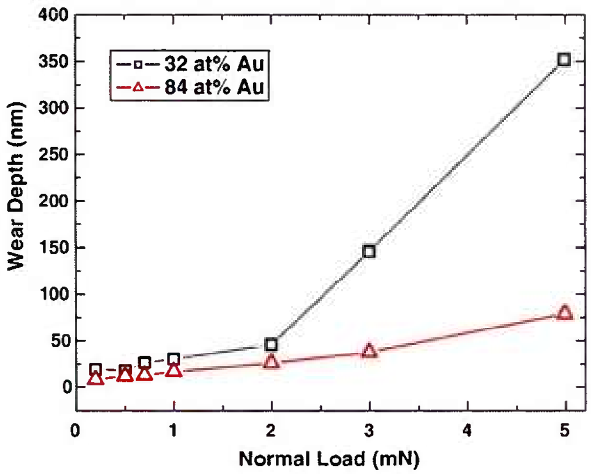

Fig. 5. Wear depth, measured after 800 cycles, versus normal load.

310 nm coating thickness. This would indicate that wear of the Si substrate had commenced prior to the end of the test.

4. Discussion

From the friction and wear results with normal loads below 2.0 mN, both coatings have similar performance for the 800 cycles tested. While the 32% Au coating had slightly greater wear, this difference was minimal. When the normal load was increased, the performance changed significantly, with the 32% Au coating having much greater wear than the 84% Au coating. At the same time, the friction coefficient increased for the 32% Au specimen.

To consider the mechanisms for these differences in performance, an examination of the friction behavior with normal load was conducted that consisted of non-linear curve fitting with Eq. (1). For all of the data collected, the curve fitting results of friction coefficient data versus normal load yield curves qualitatively similar to those shown in Fig. 2. While two extremes are shown in Fig. 2 for primarily elastic and strongly affected by plowing, other data sets fell somewhere in between. These differences are most readily seen by plotting the two contributions to the total friction coefficient, μ_e and μ_p, separately. In this way, the evolution of the sliding process versus normal load or time may be explored. It should be noted that data used for this analysis were taken from the end of each test cycle, where the effect of the friction rises observed in Figs. 3 and 4 was minimized.

To explore the evolution of the sliding process with time, μ_e and μ_p were plotted versus cycles. These results are plotted in Fig. 6 for three normal loads (1.0, 3.0 and 5.0 mN). For all three loads, the elastic component for the 32% Au coating dropped during the run-in portion of the tests and then remained relatively constant (Fig. 6(a)). For the higher loads of 3.0 and 5.0 mN, the plastic component rose steadily throughout the test. For the 5.0 mN load, the plastic component becomes greater than the elastic early in the test (<100 cycles). For the 3.0 mN load, this crossover occurs much later, at approximately cycle 600. While this crossover was not observed for a load of 1.0 mN, the curve for μ_p is steadily rising throughout the test, perhaps an indication that even at this load, the 32% Au coating will eventually fail. For the 84% Au coating (Fig. 6(b)), the plowing component drops during run-in and then remains nearly constant. At the same time the elastic component rises slightly at the start of the test and then also stays nearly constant. This evolution was observed for all normal loads and could be considered indicative of the steady state sliding taking place. There is a slight rise in μ_p with increasing cycle, possibly indicating that wear does progress for these coatings.

Observations from Fig. 6 are consistent with coating wear measurements (Fig. 5). For the 84% Au coating, wear was minimal at all loads compared to the 32% Au coating. The 84% Au coating had nearly constant values of μ_e and μ_p with increasing cycles, and the plowing friction was always significantly smaller than the elastic component. When the 32% Au coating did not fail (at smaller normal loads), μ_e and μ_p were constant after run-in. When significant wear was observed, the plastic component steadily rose throughout the test. Combining the observations from curve fitting of friction data and post-test wear analysis, it appears that sliding on the 84% Au coating results in a quick formation of a transfer film that remains stable throughout the test. At small loads, the same can be said for the 32% Au coating. However, at higher loads, the sliding on the 32% Au coating results in a plowing process. This plowing leads to coating wear and may also be associated with failure of the transfer films. Future work will explore these hypotheses. However, this discussion is consistent with differences in the coatings themselves. Higher metal content typically provides a harder, more fully dense coating that leads to thinner, more stable transfer films. Pure or lightly doped MoS_2 coatings are typically softer and will form patchy transfer films [9] that can lead to wear-related velocity accommodation modes [2,12], such as plowing.

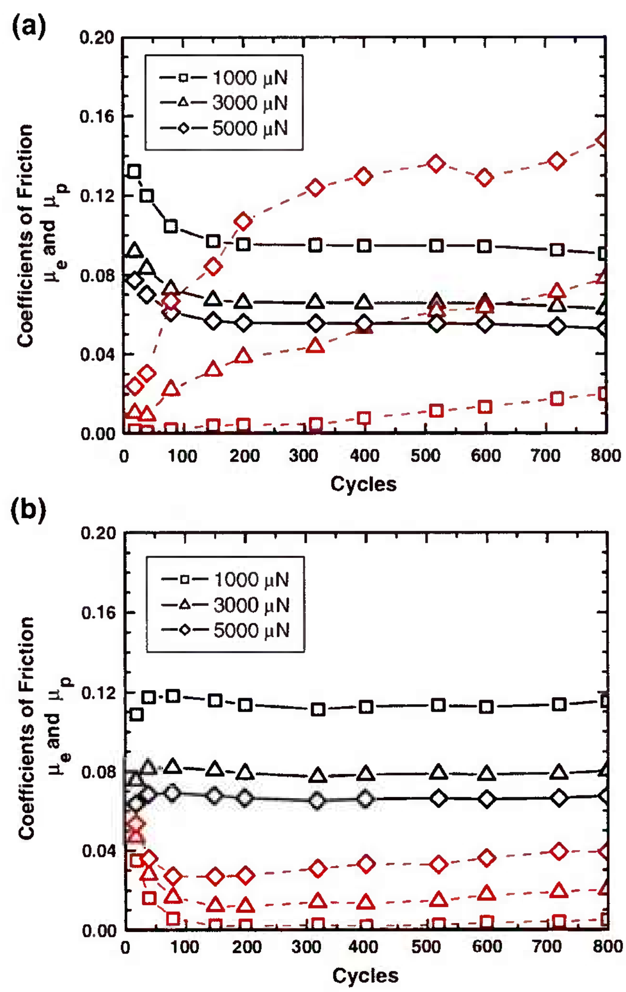

Fig. 6. Calculated coefficients of friction, μ_e (solid lines) and μ_p (dashed lines), versus cycle number for the 32 at.% Au coating (a) and the 84 at.% Au coating (b). These plots were constructed from the fitting results similar to those shown in Fig. 2, where the best fit parameters were used to calculate the elastic and plastic contribution to the total friction coefficient.

5. Conclusions

Microtribology experiments on Au–MoS_2 coatings in dry environments showed that a higher Au content coating (84 at.%) resulted in less wear and a more stable friction coefficient compared to a 32 at.% Au coating. Calculated values for the elastic (μ_e) and plastic (μ_p) components of the friction coefficient, obtained from non-linear curve fitting, were found to evolve with time. When coating wear was minimal, both μ_e and μ_p remained relatively constant after a reduction in the plastic component during run-in. When coating wear was significant, μ_e decreased and μ_p increased with increasing time.

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